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P100899GB

Patent application number (The Patent Office will fill in this part) 0225648.5

Full name, address and postcode of the or of each applicant (underline all sumames)

Doncasters Limited Paralloy House **Nuffled Road** Billingham TS23 4DA United Kingdom

Patents ADP number (if you know to)

If the applicant is a corporate body, give the country/state of its incorporation

United Kingdom

4. Title of the invention

HIGH TEMPERATURE ALLOYS

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Robert Leonard HALL

Harrison Goddard Foote Fountain Precinct Leopold Street Sheffield, S1 2QD UNITED KINGDOM

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7914237001

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Country

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DUPLICATE

High Temperature Alloys

This invention relates to high temperature alloys, and more particularly to an oxide dispersion strengthened nickel-chromium-iron alloy having improved creep resistance and oxidation resistance at high temperatures.

Frequently alloy materials for use at high temperatures, for example, alloy tubes used in ethylene pyrolysis and in steam methane reforming, suffer from insufficient 10 creep resistance. The industry continues to look for improved materials and other technologies to enable more efficient ethylene production under increasingly severe pyrolysis/cracking conditions (higher temperatures, shorter residence times, and lower partial pressures of 15 product), leading to increased ethylene yields. Current alloys have specific issues related to their creep performance which causes failure at increasingly high design process temperatures. This is the case currently for both castable alloy tubes and wrought alloy tubes. 20

An example of a known alloy material is INCOLOY® alloy.
803 (UNS S 35045), which is an iron-nickel-chromium alloy
specifically designed for use in petrochemical, chemical
and thermal processing applications. The composition of
INCOLOY 803, by weight, is 25%Cr, 35%Ni, 1%Mn, 0.6%Ti,
0.5%Al, 0.7%Si, 0.07%C and balance Fe. Relatively
unsuccessful efforts have been made to improve the
properties of this alloy by the addition of further
alloying components and also by cladding.

It has been known for about thirty years that alloy creep resistance can be considerably improved by adding a fine dispersion of oxide particles into a metallic matrix,

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yielding a so-called oxide dispersion strengthened (ODS) alloy. Such alloys show a creep threshold, that is to say, below a certain stress their creep rate is very low. This behaviour is commonly explained by interfacial pinning of the moving dislocations at the oxide particle; Bartsch, M., A. Wasilkowska, A. Czyrska-Filemonowicz and U. Messerschmidt Materials Science & Engineering A 272, 152-162 (1999). It has recently been proposed to provide oxide dispersion strengthened clad tubes based on INCOLOY 803, but to date no entirely successful commercial product is available

(www.oit.doe.gov/imf/factsheets/mtu tubes).

According to the present invention, an improved creep 15 resistant nickel-chromium-iron alloy comprises up to about 5% of hafnium-containing particles. The alloy is particularly useful in the production of creep resistant tubes.

Also according to the invention, an improved oxide dispersion strengthened nickel-chromium-iron alloy is provided, which comprises up to about 5% of hafnium, with at least part of the hafnium being present as finely dispersed oxidised particles.

In a first aspect, the present invention provides an oxide dispersion strengthened nickel-chromium-iron alloy comprising, by weight:

30 Carbon 0.01 - 0.5% Silicon 0.1 - 2.5% Manganese 0 - 2.5% Nickel 15 - 50% Chromium 20 - 40% 35 Molybdenum 0 - 1.0%

	Niobium	0 - 1.7%
	Titanium	0 - 0.5%
	Zirconium	0 - 0.5%
	Cobalt	0 - 2.0%
5	Tungsten	0 - 1.0%
	Hafnium .	0.01 - 4.5%

balance iron and incidental impurities,

with the proviso that at least one of miobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

In a second aspect, the present invention provides a method of manufacturing an oxide dispersion strengthened nickel-chromium-iron alloy which comprises adding finely divided hafnium particles to a melt of the alloy before pouring, under conditions such that at least part of the hafnium is converted to oxide in the melt.

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Preferred alloys according to the invention include the following compositions, where all percentages are given by weight:

	Carbon	Silicon	Manganose	Nickel	Chromium	Molybdenum
A.	0.3 - 0.5	0.1 - 2.5	2.5:max	30-40 .	20-30	1.0 max
В	0.03 - 0.2	0.1 - 2.5	2.5 max	30-40	20-30	1.0 max
С	0.3 - 0.5	0.1-2.5	2.5 max	40 – 50	30-40	1.0 max
D	0.03 - 0.2	0.1 - 2.5	2.5 max	40 – 50	30-40	1.0 max
E	0.30 - 0:5	0.1 - 2.5	2.5 max	19 – 22	24 – 27	1.0 max
F	0.03 - 0.2	0.1-2.5	2.5 max	30 - 45	19 – 22	1.0 max

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	Niobium	Hafnium	Titanium	Zirconium	Cobalt	Tungsten
A	1.7 max	0.025 - 4.5	0.5 max	0.5 max ·	2.0 max	1.0 max
В	1.7 max	0.025 - 4.5	0.5 max	0.5 max	2.0 max	1.0 max
C	1.7 max	0.025 - 4.5	0.5 max	0.5 max	2.0 max	1.0 max
D	1.7 max	0.025 - 4.5	0.5 max	0.5 max	2.0 max	1.0 max
E	1.7 max	0.025 - 4.5			2.0 max	1.0 max
F	1.7 max	0.025 - 4.5	0.5 max	0.5 max	2.0 max	1.0 max

balance iron and incidental impurities.

The amount of hafnium in the alloy, by weight, is preferably from 0.05 to 3.0%, more preferably from 0.1% to 1.0% and most preferably from 0.2 to 0.5%. Preferably the hafnium is present in the alloy in the form of finely divided oxidised particles having an average particle size of from 50 microns to 0.25 microns, or less, more preferably from 5 microns to 0.25 microns or less.

A particularly preferred alloy composition according to the invention consists essentially of the following components, by weight:

	Carbon	0.45%
	Silicon	1.3%
	Manganese	0.9%
	Nickel	33.8%
20	Chromium	25.7%
	Molybdenum	0.03%
	Niobium	0.85%
	Hafnium	0.25%
	Titanium	0.1%
25	Zirconium	0.01%
	Cobalt	0.04%
	Tungsten	0.01%
	Iron	balance.

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Incidental impurities in the alloys of the invention can comprise, for example, aluminium, phosphorus, sulphur, vanadium, zinc, arsenic, nitrogen, tin, lead, copper and cerium, up to a total amount of about 1.0%.

In the method of the invention, it is important to provide conditions in the melt which permit oxidation of hafnium particles without allowing detrimental reactions which would result in the hafnium being taken up in the slag. The correct oxidising conditions can be achieved by appropriate adjustment or additions of the components, especially silicon, and by ensuring that unwanted contaminants such as aluminium are absent or kept to a minimum. If the slag is able to react with the oxidised hafnium particles this of course removes them detrimentally from the melt. The level of oxygen in the melt can be varied by micro-additions of, for example, one or more of silicon, niobium, titanium and zirconium, and the optimum free oxygen level necessary to react with the hafnium particles can readily be found by routine experimentation.

After the reaction of the hafnium particles with free oxygen, alloying amounts of titanium and/or zirconium may 25 be added, up to the specified limits of 0.5% by weight. The substantial removal of available free oxygen from the melt helps to ensure that any such titanium and zirconium form additions do not oxides, which could detrimentally with the hafnium particles and reduce the 30 yields of titanium, zirconium and hafnium present in the alloy.

It is important that the hafnium is added to the melt as finely divided particles and that it is oxidised in situ.

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to add large pieces of Attempts hafnium to nickel/chromium micro-alloys have revealed that hafnium does not disperse, but settles to the bottom of the alloy melt, or reacts with carbon resulting in a decrease of the alloy properties. Surprisingly, we have also found that, the addition of hafnia (hafnium oxide) particles directly to the melt does not provide the desired dispersion strengthening either. Hafnia added in this way simply goes into the slag. According to the invention it has been found that it is necessary to carry out the oxidation of the hafnium particles in the melt in order to obtain the desired improvement.

The charge make up can be a virgin charge (pure metals), a mixture of virgin charge and reverts, a mixture of 15 virgin charge and ingots, or a mixture of virgin charge and reverts and ingots. The ingots can be made from argon/oxygen decarburisation (AOD) revert alloy treatment or from in-house reverts treated by argon purging. each case the chemical composition of the melt should be 20 carefully monitored ±φ avoid contaminants formation of unwanted slag. Special care should be taken to deslag the bath, and the maximum amount of slag is preferably removed from the surface of the bath. It is possible to improve slag removal by the use of a neutral -25 deslag powder. If desired the melt can be maintained in . an argon atmosphere, but this is not essential.

The melt temperature is preferably in the range of from 30 1580°C to 1700°C, preferably from 1610°C to 1670°C.

Hafnium particles are preferably added to the melt just before pouring the molten alloy into the mould. If a ladle is used, the hafnium is preferably added in the

To improve the hafnium dispersion, the molten ladle. alloy is preferably stirred before pouring.

Any type of hafnium can be used, but electrolytic hafnium is preferred. The hafnium particles are preferably reduced in size as much as possible, for example, by grinding to a fine powder in a suitable mill. The hafnium particles preferably have a particle size of less than 5 mm, preferably less than 4 mm, with an average of from I to 2 mm. When dispersed in the melt, the hafnium particles are further reduced in size.

alloys of the invention have a primary carbide network similar to the corresponding alloys without the dispersion. The primary carbides oxide are of chromium and/or iron composed carbo-nitrides. optionally with niobium, titanium and/or zirconium carbonitrides also present. The invention also provides the possibility of obtaining a dispersion of 20 carbides after the alkoy has been brought to a high temperature. These secondary carbides are mainly chromium (or other elements such as iron) carbo-nitrides optionally niobium, titanium (and/or zirconium) nitrides.

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In additions to these precipitates, the invention provides for the formation of a hafnia / hafnium oxide dispersion (the hafnium can be oxidised to form HfO2, but it can be expected that there will also be formed an oxide HfO_x with x as a variable), carbo-nitrides hafnium/niobium/titanium and oxides mixtures (the quantity of niobium and titanium is variable as well as the nitrogen and the oxygen). also possible that some hafnium carbo-nitrides may be formed. More numerous titanium nitride (or carbide)

dispersions may be observed in the alloy, some of which may also contain hafnia particles.

The alloys of the invention have improved temperature creep resistance, leading to an 5 improved service life expectancy. Without wishing to be confined to any particular theory, it is believed that the creep resistance of the new alloys derives from the ability of the particle dispersion to delay the motion of the dislocations in the alloy lattice. The micro-alloy, without the oxide dispersion, can delay the motion of dislocations by the presence of carbide (and/or nitride) precipitates, but the presence of the oxide dispersion provides a substantial unexpected extra improvement.

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The alloys of the invention can be formed into tubes, for example, by rotational moulding, and such rotationally moulded tubes are a further aspect of the invention. rotational moulding process can provide a non-uniform particle distribution in the tube wall, with the greater concentration of particles being towards the surface of the tube wall, and this can be beneficial in some cases. For example, in certain applications the internal bore of the tube is machined, removing 4-5 mm of material; this gradient of concentration ensures that the hafnium/hafnia reinforcement is kept in the useful part Other components that can be manufactured of the tube. from the new alloys include fittings, fully fabricated ethylene furnace assemblies, reformer tubes and manifolds.

A further advantage of the hafnium addition is that it can tend to improve the oxide layer adherence at the surface of an alloy tube. The alloy is able to develop an oxide layer on its surface that protects it against

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corrosion by carburisation. This protective oxide layer is formed ideally of chromium/manganese/silicon oxides, but can also include iron and nickel oxides. The oxide layer has a tendency to spall during the tube service life (because of differences of coefficients of expansion with the alloy, compressive stresses in the oxide, etc). Spalling leaves the alloy unprotected against corrosion from the gaseous and particulate reactants of the ethylene cracking process. It has surprisingly been found that the hafnium addition can tend to delay the spalling of the protective oxide layer.

Embodiments of alloys according to the invention are illustrated in the accompanying Drawings, by way of example only, in which:

Figure 1 is a photomicrograph of a first alloy according to the invention with its composition:

Figure 2 is a photomicrograph of a second alloy according to the invention with its composition;

Figure 3 is a photomicrograph of a third alloy according to the invention with its composition; and

Figure 4 is a photomicrograph of a fourth alloy acording. to the invention with its composition.

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The invention is further illustrated by the following Examples, in which all percentages are by weight:

Example 1

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The following melt composition is produced in a clean furnace:

Nickel 25%

35 Chromium 35%

Carbon 0.4%

Niobium 0.8 - 0.9%

Silicon 1.6 - 1:8%

Manganese 1.1 - 1.3%

5 Iron balance.

The temperature of the melt is raised to a tap temperature of 1640°C to 1650°C and the silicon content checked. The furnace is then de-slaged, removing as much slag as possible. 100kg of alloy are then tapped into a ladle and 0.35% hafnium particles of particle size maximum 5 mm, average 1 -2 mm, are added to the tap stream. After the hafnium addition, 0.18% titanium, in the form of FeTi is added to the ladle.

The alloy in the ladle is stirred and immediately poured into a tube mould.

The creep resistance properties of the alloy thus
20 produced were compared with the properties of an
otherwise identical commercial alloy from which the
hafnium addition was omitted.

The results of a Larson-Miller plot of the stress-rupture properties of the commercial alloy derived from the regression analysis of numerous creep tests gave a typical figure of 16.7 MPa at a temperature of 1100°C. The commercial alloy is expected to fail after a minimum of 100 hours, with a mean value failure of 275 hours.

30 The alloy according to the invention had a minimum failure time of rupture of 370 hours and a mean value failure of 430 hours.

Example 2

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The procedure of Example 1 is repeated using the same melt composition except that the titanium addition is omitted.

- The creep resistance properties of the alloy thus produced were compared with the properties of an otherwise identical commercial alloy from which the hafnium addition was omitted.
- The results of a Larson-Miller plot of the stress-rupture properties of the commercial alloy derived from the regression analysis of numerous creep tests gave a typical figure of 16.2 MPa at a temperature of 1100°C. The commercial alloy is expected to fail after a minimum of 100 hours, with a mean value failure of 202 hours. The alloy according to the invention had a minimum failure time of rupture of 396 hours, a mean value failure of 430 hours and a maximum failure time of rupture of 629 hours.

The results of Examples 1 and 2 show the dramatic improvement in creep properties that can be obtained using the alloys and method of the invention.

25 The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination,

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except combinations where at least some of such features and/or steps are mutually exclusive.

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

The invention is not restricted to the details of any foregoing embodiments. The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

CLAIMS

1. An oxide dispersion strengthened nickel-chromium-5 iron alloy comprising, by weight:

	Carbon	0.01 to 0.5%
	Silicon	0.01 to 2.5%
	Manganese	0 to 2.5%
10	Nickel	15 to 50%
	Chromium	20 to 40%
	Molybdenum	0 to 1.0%
	Niobium	0 to 1.7%
	Titanium	0 to 0.5%
15	Zirconium	0 to 0.5%
	Cobalt	0 to 2.0%
	Tungsten	0 to 1.0%
	Hafnium	0.01 to 4.5%,

20 balance iron and incidental impurities, .

with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finally divided oxide particles.

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2. An alloy according to claim 1 having the following composition, by weight:

	Carbon	0.3 to 0.5%
30	Silicon	0.1 to 2.5%
	Manganese	2.5% max.
	Nickel	30 to 40%
	Chromium	20 to 30%
	Molybdenum	1.0% max.
35	Niobium	1.7% max.

Hafnium 0.01 to 4.5%
Titanium 0.5% max.
Zirconium 0.5% max.
Cobalt 2.0% max.
5 Tungsten 1.0% max.,
Balance iron and incidental impurities.

3. An alloy according to claim 1 having the following composition, by weight:

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Carbon 0.03 to 0.2% Silicon 0.1 to 0.25% Manganese 2.5% max. 30 to 40% Nickel 20 to 30% 15 Chromium 1.0% max. Molybdenum Niobium 1.7% max. Hafnium 0.01 to 4.5% Titanium 0.5% max. 20 Zirconium 0.5% max. Cobalt 2.05% max. Tungsten 1.0% max.,

balance iron and incidental impurities.

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4. An alloy according to claim 1 having the following composition, by weight:

0.3 to 0.5% Carbon 0.1 to 2.5% 30 Silicon 2.5% max. Manganese Nickel 40 to 50% 30 to 40% Chromium Molybdenum 1.0% max. 1.7% max. 35 Niobium

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Hafnium 0.01 to 4.5%
Titanium 0.5% max.
Zirconium 0.5% max.
Cobalt 2.0% max.
Tungsten 1.0% max.,

balance iron and incidental impurities.

5. An alloy according to claim 1 having the following 10 composition, by weight:

Carbon 0.03 to 0.2% Silicon 0.1 to 2.5% Manganese 2.5% max. 15 Nickel 40 to 50号 Chromium 30 to 40% Molybdenum 1.0% max. Niobium 1.7% max. 0.01 to 4.5% Hafnium 20 Titanium. 0.5% max. Zirconium 0.5% max. Cobalt 2.0% max. Tungsten 1.0% max.,

- 25 balance iron and incidental impurities.
 - 6. An alloy according to claim 1 having the following composition, by weight:
- 30 Carbon 0.3 to 0.5% Silicon 0.1 to 2.5% Manganese 2.5% max.

 Nickel 19 to 22% Chromium 24 to 27%
- 35 Molybdenum 1.0% max.

Niobium 1.7% max
Hafnium 0.01 to 4.5%
Cobalt 2.0% max.
Tungsten 1.0% max.,

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balance iron and incidental impurities.

7. An alloy according to claim 1 having the following composition, by weight:

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Carbon 0.03 to 0.2% Silicon 0.1 to 2.5% Manganese 2.5% max Nickel 30 to 45% 15 Chromium 19 to 22% Molybdenum 1.0% max. Niobium 1.7% max. Hafnium 0.01 to 4.5% Titanium 0.5% max. 0.5% max. 20 Zirconium Cobalt 2.0% max. Tungsten . 1.0% max.,

balance iron and incidental impurities.

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- 8. An alloy according to any of the preceding claims, in which the amount of hafnium in the alloy, by weight, is from 0.01 to 3.0%.
- 30 9. An alloy according to any of the preceding claims, in which the amount of hafnium in the alloy, by weight, is from 0.1% to 1.0%.
- 10. An alloy according to any of the preceding claims, in which the amount of hafnium in the alloy, by weight,

is from 0.2 to 0.5%.

- 11. An alloy according to any of the preceding claims, in which the hafnium is present in the alloy in the form of finally divided oxidised particles having an average particle size of from 50 microns to 0.25 microns, or less.
- 12. An alloy according to any of the preceding claims,

 10 in which the hafnium is present in the alloy in the form

 of finally divided oxidised particles having an average

 particle size of from 5 microns to 0.25 microns, or less.
- 13. An alloy having the following composition, by 15 weight:

	·Carbon	U.45%
	Silicon	1.3%
	Manganese	.0.9₺
20	Nickel	33.8%
	Chromium	25.7%
	Molybdenum	0.03%
	Niobium	0.85%
	Hafnium	0.25%
25	Titanium	0.1%
	Zírconium	0.01%
	Cobalt	0.48
	Tungsten '	0.01%,

Carbon

30 balance iron and incidental impurities.

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- 14. An alloy according to any of the preceding claims substantially as described in the Examples.
- 35 15. A nickel-chromium iron alloy comprising up to about

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5% of hafnium-containing particles.

- 16. A method of manufacturing an oxide dispersion strengthened nickel-chromium-iron alloy which comprises adding finely divided hafnium particles to a melt of the alloy before pouring, under conditions such that at least part of the hafnium is converted to oxide in the melt.
- 17. A method according to claim 16, in which the alloy is an alloy as claimed in any of claims 1 to 15.
 - 18. A method according to claim 16 or 17, wherein the hafnium particles have a particle size of less than 5mm.
- 15 19. A method according to any of claims 16 to 18, in which the amount of hafnium added to the melt is from 0.01 to 3.0% by weight.
- 20. A method according to any of claims 16 to 19, 20 wherein the hafnium particles are added to the melt shortly before pouring the molten alloy into the mould.
 - 21. A method according to claim 20, in which the hafnium particles are added to the molten alloy in a ladle.
- 22. A method according to any of claims 16 to 21, in which the hafnium is electrolytic hafnium.
- 23. A method according to any of claims 16 to 22, in 30 which the alloy melt is substantially aluminium free.
 - 24. A method according to any of claims 16 to 23, wherein the level of oxygen in the melt is varied by additions of one or more of niobium, titanium and zirconium.

25. A method according to claim 24, in which the titanium is added in the form of TiFe after the hafnium addition.

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- 26. A method according to any of claims 16 to 24, in which the maximum amount of slag is removed from the surface of the alloy.
- 10 27. A method according to any of claims 16 to 26, in which the melt temperature is in the range of from 1580°C to 1700°C.
- 28. A method according to any of claims 16 to 27, in 15 which the alloy is formed into a tube by rotational moulding.
 - 29. A method according to any of claims 16 to 28 substantially as described in the Examples.

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- 30. A method of manufacturing a nickel-chromium-iron alloy, which comprises adding finely divided hafnium particles to the melt before pouring.
- 25 31. A creep resistant alloy tube formed from a nickelchromium-iron alloy comprising up to about 5% of hafniumcontaining particles.
- 32. A tube according to claim 31, which comprises an oxide dispersion strengthened nickel-chromium-iron alloy comprising up to about 5% of hafnium
- 33. A nickel-chromium-iron alloy tube comprising up to about 5% of hafnium-containing particles substantially as hereinbefore described.

- 34. A tube formed from an alloy according to any of claims 1 to 15 by rotational moulding.
- 5 35. A nickel-chromium-iron alloy having a structure and composition substantially as described and illustrated in Figures 1 to 4 of the accompanying Drawings, wherein the tables represent percentages by weight of the alloy constituents.

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ABSTRACT

An improved creep resistant nickel-chromium-iron alloy comprises up to about 5% of hafnium-containing particles.

In one embodiment, an improved oxide dispersion strengthened nickel-chromium-iron alloy is provided, which comprises up to about 5% of hafnium, with at least part of the hafnium being present as finely dispersed oxidised particles.

10 The alloy is particularly useful in the production of creep resistant tubes.

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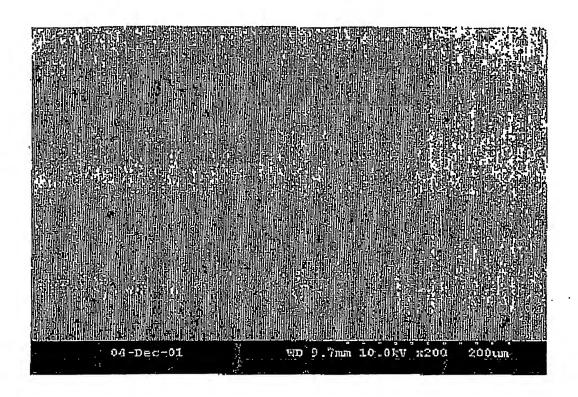


Figure 1

С	Si	Mn	Ni	Cr	Mo	Nb	Нf	Ti	Zr	Co	W
0.41	1.12	0.73	34.3	25.7	0.02	0.96	0.26	0.00	0.008	0.05	0.01

Traces (AI + P + S + V + Zn + As + N + Sn + Pb + Cu + Ce) = 0.31

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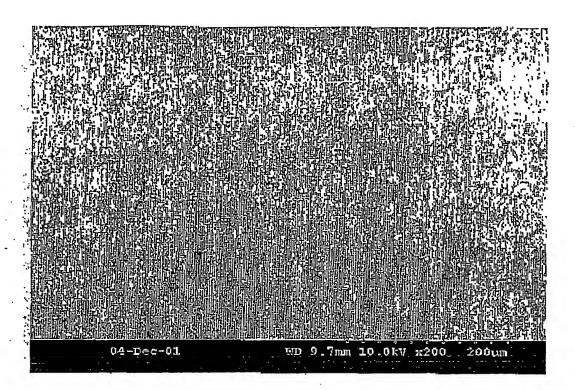


Figure 2

. إ	С	Si	Mn	Ni	Cr	Мо	Nb	Hf.	ĽĮ.	Zr	Co	W
	0.41	1.85 ;	1.47	34.7	24.4	0.05	0.96	0.10	0.09	0.01	0.04	0.02

V + Zn + As + N + Sn + Pb + Cu + Ce) = 0.32

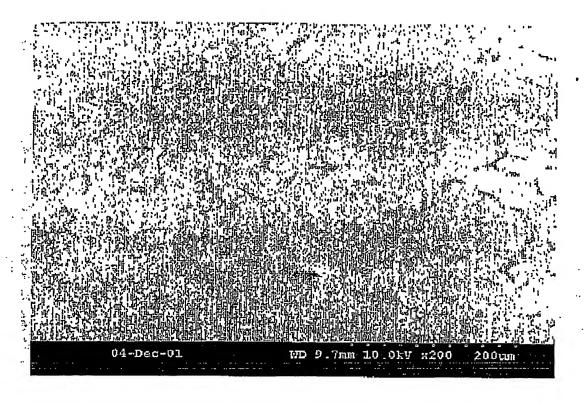


Figure 3

C	-Si	Mn	Νì	Cr	, Mo	Мb	:: Hf	Ti	Zr	; Co	W
0.40	1.51	0.96	33.2	24.7	0-02	0.77	0.31	O.OB	0.01	0.05	0.01

Traces (AI + P + S + V + Zn + As + N + Sn + Pb + Cu + Ce) = 0.28

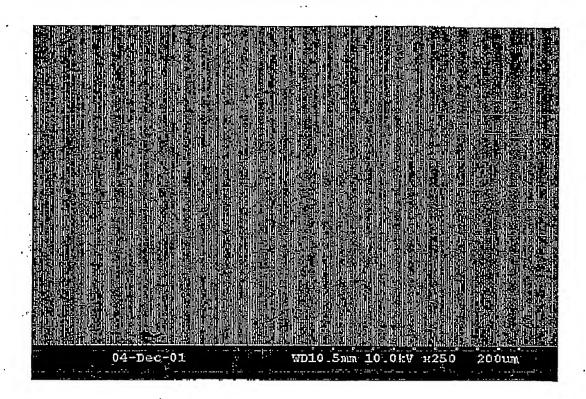


Figure 4

С	Si	Mn	Ni	Cr	Mo	Nb	нf	Ti	Zr	Co	พ์
0.45	1.30	0.90	33.8	25.7	0.03	0.85	0.25	0.10	0.01	0.04	0,01

Traces (AI + P + S + V + 2n + As + N + Sn + Pb + Cu + Ce) = 0.29